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(54) A method for forming a thin film and semiconductor devices.

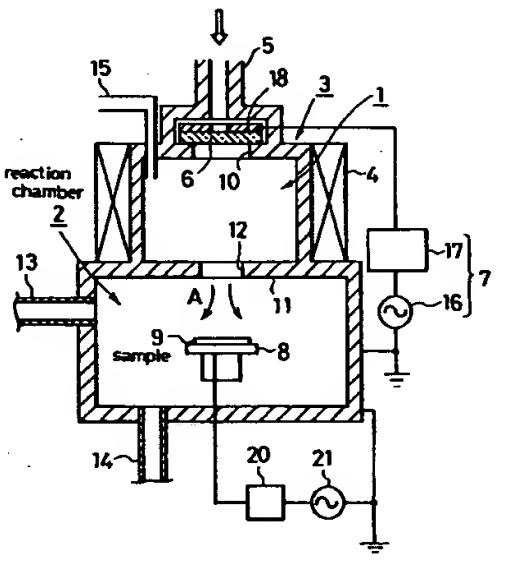
(57) A method for forming a thin film, comprising the steps of:

generating a plasma in a plasma generation chamber by action of an electric field generated by a microwave and a magnetic field generated by an exciting coil arranged around; and

introducing the generated plasma into a reaction chamber, resulting in forming a thin film on a sample placed on a sample stage, wherein it is a chracteristic to form a metal nitride film on said sample, by introducing Ar, H_2, and N_2 gas into said plazma generation chamber, while introducing a metallic gas into said reaction chamber.

By the method according to the present invention, it is possible to form a thin film having good Step Coverage on the contact hole, in addition, on the side wall of the contact hole a thinner film can be formed than that on the bottom. As a result, in the next step, filling in with interconnection materials can be surely performed, resulting in improving reliability of LSI devices.

FIG. 1



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The present invention relates to a method for forming a thin film and semiconductor device and more particularly to a method for forming a thin film, such as TiN film formed as a barrier layer on the inside surface of a contact hole in a Semiconductor device and to the semiconductor device in which said thin film was formed.

A contact section in a semiconductor device such as LSI, has a diffusion layer on the surface of a substrate as a base, connected with an interconnection such as Al through a contact hole.

However, as LSI gets further finer and more highly integrated, a diffusion layer formed on the surface of a substrate becomes shallower. Such problems arise as in said shallow diffusion layer, Al spike occurs and destroys a connection or Si deposits on the bottom of the contact hole, which results in increasing contact resistance.

In order to solve these problems, Al alloys (e. g. Al-1%Si) previously contaminated with about 0.5-2% of Si are used as electrode connection material, but even these Al alloys are recently insufficient to prevent deposition of Si as a diameter of a contact hole is smaller than before.

Accordingly, forming a thin film called a barrier metal between Al alloy and a Si substrate for prevention of diffusion is considered. A TiN film is known as a barrier metal on account of its small electrical resistance and chemical stability (Yamanishi, Yoshihara, Kitahara, and Hosokawa; "Vacuum", Vol.30 No.5 P347, 1987).

A TiN film was so far formed by Reactive Sputtering method. The Reactive Sputtering method is how to form a TiN film on a substrate 31 by using Ti as a target 30 and providing Ar and N_2 as sputtering gas in such an device as shown in Fig.21 (Kanamori; "Vacuum", Vol.29 No .9 P418, 1986). Reference numeral 32 designates a coil.

However, by this method, wherein Step Coverage is poor, a TiN film is formed in the contact section as shown in Fig. 22(a). As a semiconductor device gets more highly integrated to 64MDRAM, and next to 256MDRAM, aspect ratio (=hole depth / hole diameter) of contact hole 3, becomes gradually higher. As a result, by this method almost no TiN film is formed on the bottom of a contact hole 35, so that it becomes impossible to use this method. In other words, even if in a state shown in Fig. 22(a) electrode material such as W(tungsten) or Al is filled in, a void 36 occurs inside the contact hole 35, wherein interconnection becomes easy to be broken, resulting in losing function as a barrier metal, so that it is impossible to maintain reliability of LSI devices produced.

Accordingly, LPCVD method (Low Pressure Chemical Vapor Deposition method), one of thermal CVD methods, began to be known as a method for forming a thin film having good Step Coverage. This method is how to form a TiN film on a substrate by thermal reaction with using $TiCl_4$, and NH_3 or N_2 gas as materials in such an device as shown in Fig.23 (N.Yokoyama et al., Vol.136 No.3, J.Electrochem.Soc., P882)(N.Yokoyama et al.,Vol.138 No.1, J.Electrochem.Soc., P190).

However, as the formation of a TiN film by reaction of $TiCl_4 + N_2 + H_2$ requires high temperature of about 900~1000°C, resulting in having a bad influence on device characteristics, the method had a problem that it cannot be applied to production of a LSI device (Arthur Sherman, Extended Abstract of the 1991 International Conference on Solid State Devices and Materials, 1991 P177~179).

On the other hand, as reaction of $TiCl_4 + NH_3$ takes place at low temperature, a method wherein NH_3 gas is used was promising for forming a barrier metal for a LSI device. However, it was a problem that $TiCl_4$ and NH_3 forms a Complex ($TiCl_4 \cdot nNH_3$) in vapor-phase, which turns yellow powder, resulting in generation of particles (M.J.Buiting, et al., J.Electrochem.Soc., Vol.138, No.2, Feb. 1991 P500). Besides, by the LPCVD method, a TiN film is comformally formed in a contact section as shown in Fig.24(a). In case of the formation by the LPCVD method, a TiN film 33 is sufficiently formed on the bottom of a contact hole 35, which is preferable as a barrier metal; however, simultaneously a TiN film of the same thickness as that on the bottom of the contact hole 35 is formed on the side wall of the contact hole. The formation of a thick film of TiN on the side wall like this, results in a small diameter of a hole remained in the contact hole 35; substantially it is the same situation in which a contact hole of big aspect ratio is formed. Consequently, in the next step, when W(tungsten) or Al and the like filled in, a void 36 occurs in the contact hole 35 as shown in Fig.24(b); it is another problem so as to maintain reliability of a LSI device.

In the LPCVD method, such an device as shown in Fig.23 is used as mentioned above. Reference numeral 40 designates a chamber, wherein a gas nozzle 41 and a sample stage 42 are arranged, and on the sample stage 42, a substrate 43 is placed. The bottom of the chamber 40 is connected with a booster pump 44 and a rotary pump 45, and the gas nozzle 41 is connected with a pipe 47 for NH_3 gas supply.

In consideration of the above-mentioned problems, the present inventors studied to accomplish the following invention.

That is, the present invention chiefly consists of using Ar, H_2, N_2 gas and a metallic compound gas, generating a plasma in a plasma generation chamber by action of electric field generated by a microwave and a magnetic field generated by an exciting coil arranged around, and introducing the generated plasma into a reaction chamber, resulting in forming a thin film of metal nitride on a sample placed on a sample stage.

By this method, to form a thin film having good Step Coverage in a contact hole, and in addition to make thickness of a thin film formed on the side wall of a contact hole thinner than that on the bottom of the contact hole is an object of the present invention.

Moreover, it is another object of the present invention to provide a method for forming a thin film at low temperature having no bad influence on a LSI device, and in addition, producing no particles such as yellow powder.

Fig. 1 is diagrammatic sectional view showing an example of thin film formation device according to the present invention;

Fig. 2 is diagrammatic sectional view showing another example of thin film formation device;

Fig. 3 is a graph indicating the relationship between flow rate of $TiCl_4$ gas and deposition rate, and the relationship between flow rate of $TiCl_4$ gas and film resistivity;

Fig. 4 is a graph indicating the relationship between aspect ratio of a contact hole and hole bottom / hole outside surface deposition rate;

Fig. 5 is a sectional view showing the state of a TiN film formed on the inside surface of the contact hole under the conditions of $TiCl_4$: 10SCCM and gas pressure : 1.3 mTorr;

Fig. 6 is a sectional view showing the state of a TiN film formed on the inside surface of the contact hole under the conditions of $TiCl_4$: 10SCCM and gas pressure : 3 mTorr;

Fig. 7 is a sectional view showing the state of a TiN film formed on the inside surface of the contact hole under the conditions of $TiCl_4$: 10SCCM and gas pressure : 5 mTorr;

Fig. 8 is a sectional view showing the state of a TiN film formed on the inside surface of the contact hole under the conditions of $TiCl_4$: 5SCCM and gas pressure : 0.7 mTorr;

Fig. 9 (a) is a sectional view showing the state of a TiN film formed on the contact hole by the method according to the examples;

Fig. 9 (b) is a sectional view showing the state of the contact hole with W(tungsten) filled in after Fig.9 (a);

Fig. 10 is a graph indicating the relationship between film resistivity of a TiN film formed by using a plasma CVD device and substrate temperature, and the relationship between deposition rate of a TiN film and substrate temperature;

Fig. 11 is a graph indicating the relationship between film resistivity of a TiN film formed by using the plasma CVD device and microwave power, and the relationship between deposition rate of a TiN film and microwave power;

Fig. 12 is a sectional view showing the state of growth of a TiN film deposition on a Si substrate in the case of $TiCl_4$: 10SCCM;

Fig. 13 is a sectional view showing the state of growth of a TiN film deposition on a Si substrate in the case of $TiCl_4$: 5SCCM;

Fig. 14 is a sectional view showing the state of growth of a TiN film deposition on a Si substrate in the case of $TiCl_4$: 15SCCM;

Fig. 15 is a sectional view showing the state of growth of a TiN film deposition on a Si substrate in the case of $TiCl_4$: 20SCCM;

Fig. 16 is a diagram showing the result of RBS analysis of the sample which is produced by forming a TiN film on a Si substrate and evaporating Al thereon;

Fig. 17 is a diagram showing EDX spectra of a TiN film formed on Si subslrate in the case of microwave power 1kw;

Fig. 18 is a diagram showing EDX spectra of a TiN film formed Si substrate in the case of microwave power 2.8kw;

Fig. 19 is a diagram showing the result of SIMS analysis of the surface of a Si substrate on which a TiN film is formed;

Fig. 20 is a X-ray diffraction pattern of a TiN film;

Fig. 21 is a diagrammatic sectional view of a Reactive Sputtering apparatus;

Fig. 22 (a) is a sectional view showing the state of a TiN film formed on the contact hole by Reactive Sputtering method;

Fig. 22 (b) is a sectional view showing the state with W(tungsten) filled in after Fig. 22(a);

Fig. 23 is a diagrammatic sectional view showing the device used in the LPCVD method;

Fig. 24 (a) is a sectional view showing the state of a TiN film formed on the contact hole by the LPCVD method; and

Fig. 24 (b) is a sectional view showing the state with W(tungsten) filled in after Fig. 24 (a).

In more detail, a method for forming a thin film according to the present invention has characteristics as follows;

(1) in a method of generating a plasma in a plasma generation chamber by action of an electric field generated by a microwave and a magnetic field generated by an exciting coil arranged around, introducing said plasma into a reaction chamber, and forming a thin film on a sample placed on a reation chamber, by means of introducing Ar, H_2, and N_2 gas into the plazma generation chamber, while introducing a metallic compound gas into the reaction chamber forming a metal nitride film on said sample;

(2) in a method of generating a plasma in a plasma generation chamber by action of an electric field generated by a microwave and a magnetic field generated by an exciting coil arranged around, introducing said plasma into a reaction chamber, and forming a thin film on a sample placed on a reation chamber, by means of introducing Ar, H_2, N_2 gas and said metallic compound gas into the plasma generation chamber, forming a metal nitride film on said sample;

(3) in the method of forming a thin film according to (1) or (2), on a substrate for producing a semiconductor device on which an insulation film having a contact hole thereon is formed by using titanium tetrachloride gas as a metallic conpound gas, under the conditions that pressure in a reaction chamber is less than 2.0 mTorr and temperature of said substrate, a sample, is higher than 450 °C, forming a Ti nitride film on said contact hole;

(4) in the method of forming a thin film according to (1) or (2), on a substrate for producing a semiconductor device on which an insulation film having a contact hole thereon is formed, by using titanium tetrachloride gas as a metallic compound gas, under the conditions that pressure in a reaction chamber is less than 1.3 mTorr and temperature of said substrate, a sample, is higher than 450 °C, forming a Ti nitride film on said contact hole;

regarding semiconductor device according to the present invention,

(5) thickness of its Ti nitride film on the bottom of the contact hole is thicker than that on the side wall of the contact hole;

(6) thickness of its Ti nitride film is 20 ~ 60 % of that on the bottom of the contact hole;

moreover, as a for method of forming a thin film

(7) in the method according to (1) or (2), forming a film with applying RF(Radio Freguency) to a microwave inlet window;

(8) in the method according to (3), forming a film with applying RF to a microwave inlet window;

Besides,as for a semiconductor device according to the present invention,

(9) by means of introducing Ar, H_2, and N_2 gas into a plasma generation chamber, while introducing titanium tetrachloride gas into a reaction chamber, generating a plasma in the plasma generation chamber by action of an electric field generated by a microwave and a magnetic field generated by an exciting coil arranged around, and introducing the generated plasma into the reaction chamber, thickness of a Ti nitride film formed on the bottom of the contact hole became thicker than that on the side wall of the contact hole;

(10) by means of introducing Ar, H_2, N_2 gas and titanium tetrachloride gas into a plasma generation chamber, generating a plasma in the plasma generation chamber by action of an electric field generated by a microwave and a magnetic field generated by an exciting coil arranged around, and introducing the generated plasma into the reaction chamber, thickness of a Ti nitride film formed on the bottom of the contact hole became thicker than that on the side wall of the contact hole;

(11) by means of a method according to (3), thickness of a Ti nitride film formed on the bottom of the contact hole became thicker than that on the side wall of the contact hole;

(12) by means of a method according to (4), thickness of a Ti nitride film formed on the bottom of the contact hole became thicker than that on the side wall of the contact hole;

(13) by means of introducing Ar, H_2 and N_2 gas into a plazma formation chamber, while introducing titanium tetrachloride gas into a reaction chamber, generating a plasma in the plasma generation chamber by action of an electric field generated by a microwave and a magnetic field generated by an exciting coil arranged around, and introducing the generated plasma into the reaction chamber, thickness of a Ti nitride film formed on the side wall of the contact hole became 20 ~ 60 % of that on the bottom of the contact hole;

(14) by means of introducing Ar, H_2, N_2 gas and titanium tetrachloride gas into a plasma generating chamber, generating a plasma in the plasma generation chamber by action of an electric field generated by a microwave and a magnetic field generated by an exciting coil arranged around, and introducing the generated plasma into the reaction chamber, thickness of a Ti nitride film formed on the side wall of the contact hole became 20 ~ 60 % of that on the bottom of the contact hole;
(15) by means of a method according to (3), thickness of a Ti nitride film formed on the side wall of the contact hole became 20 ~ 60 % of that on the bottom of the contact hole;
(16) by means of a method according to (4), thickness of a Ti nitrite film formed on the side wall of the contact hole became 20 ~ 60 % of that on the bottom of the contact hole; and
(17) in a method according to (1) or (2), after the formation of a Ti nitride film, H_2 plasma treatment is carried out.

In other words, according to the method described in (1), Ar and H_2 gas are supplied in a plasma generation chamber so as to accelerate the film forming, while a metallic compound gas such as $TiCl_4$ is introduced into a reaction chamber, and with passing through an exciting coil supplied derect current, a microwave is introduced in the plasma generation chamber through a wave guide and a microwave inlet window.

The microwave introduced in the plasma generation chamber activates Ar, H_2 and N_2 gas supplied in the plasma generation chamber, resulting in generating a plasma. When the generated plasma is introduced into the reaction chamber by the divergent magnetic field formed by the exciting coil, said metallic compound gas reacts on said plasma, resulting in providing metal nitride on the surface of a sample placed in the reaction chamber and forming a metal nitride film thereon.

According to the method described in (2), when Ar, H_2, N_2gas and a metallic compound gas such as $TiCl_4$ are supplied in a plasma generation chamber, and with passing through an exciting coil supplied direct current, a microwave is introduced in the plasma generation chamber through a wave guide and a microwave inlet window, the microwave introduced in the plasma generation chamber activates Ar, H_2 and N_2 gas supplied in the plasma generation chamber, resulting in generating a plasma. When the generated plasma is introduced into the reaction chamber by the divergent magnetic field formed by the exciting coil said metallic compound gas reacts on N_2 and the like, resulting in providing metal nitride on the surface of a sample placed in the reaction chamber and forming a metal nitride film thereon.

As the reaction mechanism of the metal nitride film formation, the following reaction equation is considered.

$$2\,TiCl_4 + N_2 + 4\,H_2 \rightarrow 2\,TiN + 8\,HCl\uparrow$$

In order to completely decomposite $TiCl_4$ to Ti + Cl, very high energy of more than 400Kcal mol^{-1} is required.

In the method according to the present invention, by making resonance such as plasma CVD, especially electron cyclotron resonance excitation (ECR) plasma CVD occur, high energy electrons are produced, and by collision of these electrons; reactions of decomposition and reduction are enhanced.

Accordingly, without high sample temperature such as 900 ~ 1000 °C, a metal nitrite film is formed on the surface of the sample.

Ar is introduced in order to stabilize plasma discharge, and when RF is applied to the microwave inlet window in order to prevent a conductivity film from depositing on said window, Ar also acts as a sputtering gas of the conductivity film.

In the method according to the present invention, the generated plasma is supplied to the sample with good directivity, so that a metal nitride film is formed in the contact hole 35 as shown in Fig.9(a). Consequently, in the next step, when interconnction material such as W or Al is plugged up in the contact hole 35, no voids occur and plugging up is carried out as shown in Fig.9(b), resulting in achievement of flattening interconnction.

Example 1

In this example, by the plasma CVD method, the case of forming a thin film of TiN on samples having holes of different aspect ratio on the surface is described. plasma CVD apparatus used for forming a thin film according to this example.

The plasma CVD apparatus comprises a main body 3 comprising a plasma generation chamber 1 and a reaction chamber 2, an exciting coil 4 arranged around the plasma generation chamber 1 and connected with a direct current power source (not shown), a wave guide 5 introducing a microwave generated from a microwave generator (not shown) into the plasma generation chamber 1, and so on. Reference numeral 6 designates a microwave inlet window comprising a quarty glass etc., reference numeral 7 designates a radio frequency generator to apply to a radio frequency (RF) power supply on the microwave inlet window, and reference numeral 8 designates a sample stage on which a sample 9 is placed.

The plasma generation chamber 1, formed in mostly cylindrical shape with the first opening 10 for introducing a microwave formed almost at a center of the upper wall thereof , and below the plasma generation chamber 1, a reaction chamber 2 having larger diameter than the plasma generation chamber 1, are formed in one body. The reaction chamber 2 and the plasma generation chamber are devided by a diaphragm 11 with the second opening (for plasma extraction) 12 formed almost at a center thereof.

In addition, at the side wall of the reaction chamber 2 the first guide pipe 13 is connected, at the bottom of the reaction chamber 2 an exhaust pipe 14 connected with exhaust system (not shown) is connected. At the upper wall of the plasma generation chamber 1, the second guide pipe 15 is connected.

High frequency generation source 7 comprises a high frequency oscillator 16 and a matching box 17, a flat electrode 18 inserted between the microwave inlet window 6 and the wave guide 5, RF is applied to the microwave inlet window 6. The sample stage 8 is connected with a RF radio frequency oscillator 21 for applying RF radio frequency to the sample 9 through a matching box 20. Applying the prescribed radio frequency to the sample 9 by the radio frequency oscillator 21, and operating the above-mentioned method for forming a thin film, makes it possible to form a thin film having good Step Coverage even in case of high aspect ratio.

Heating the sample 9 by a fixed heater and the like and keeping the temperature of the sample 9 at the prescribed degree, such as 200 ~ 600 °C, results in accelerating crystallization of a formed thin film and low film resistivity of the thin film.

When the exciting coil 4 is supplied with direct current, the definite magnetic field is produced in the plasma generation chamber 1. As a result, it is possible to form such a magnetic field as angle frequency ω of a microwave introduced from the microwave oscillator into the plasma generation chamber 1 and angle frequency ω_c of electron cyclotron are equal in the plasma formation chamber 1, making the electrons do resonance movement. The condition under which said resonance is produced, that is ECR condition is easily determined by solving the following classical dynamic formula.

$$\omega = \omega_c = eB/m \quad ①$$

Here, e represents charge of electron ($=1.6\times 10^{-19}$C), B represents magnetic flux density (T), and m represents mass of electrons($=9.1 \times 10^{-31}$kg).

In this example angle frequency ω of a microwave was established at 2.45 GHz, and by said formula ① magnetic flux density B to fulfill the ECR condition was established at 8.75×10^{-2} T.

In order to form a thin film by using said apparatus, firstly by operating exhaust system the pressure in the main body 3 was reduced to less than 1×10^{-6} Torr, after that, while $TiCl_4$ is supplied at a flow rate of 5 ~ 15 SCCM into the reaction chamber 2 through the first guide pipe 13, Ar at a flow rate of 43 SCCM, N_2 at a flow rate of 15 SCCM, and H_2 at a flow rate of 50 SCCM, were supplied into the plasma generation chamber 1 through the second guide pipe 15. After that, the pressure in the main body 3 was established in the prescribed pressure, such as 2×10^{-3} Torr.

Moreover, turning on electricity in the radio frequency generation source 7 and applying voltage to the microwave inlet window 6, made sputtering effect by RF, by which a thin film of TiN was prevented from deposition on the microwave inlet window 6.

On the other hand, introducing a microwave of 800W from the microwave oscillator through the wave guide 5 into the plasma generation chamber 1, while connecting the exciting coil 4 with the direct current source, resulted in forming a magnetic field in the plasma generation chamber 1. Then making high energy electrons collide with material gas, which was activated to be ionized, resulting in generating a plasma.

Next, the plasma passed through the second opening 12, introduced into the reaction chamber 2 with acceleration by the divergent magnetic field to the direction of an arrow A in Fig.1, and formed a thin film of TiN on the surface of the sample 9 having a hole with aspect ratio of 0.2 ~ 1.0 placed on the sample stage 8.

The relationship between flow rate of $TiCl_4$ gas and film forming speed, and the relationship between flow rate of $TiCl_4$ gas and film resistivity obtained in this example was show in Fig. 3. As obvious from the Fig. 3, at gas flow rate of 10 SCCM, film forming speed of 700Å/min and film resistivity of 180$\mu\Omega$ cm were obtained.

Example 2

Fig. 2 is a diagrammatic sectional view showing another plasma CVD apparatus used for the method of forming a thin film according to the present invention.

As only one constructual difference of this plasma apparatus from the plasma apparatus in the example 1 is having no first guide pipe 13 connected at the side wall of the reaction chamber 2, and the other compositions are the same as the plasma apparatus in the example 1, the detailed explanation is omitted.

In order to form a thin film by using said plasma apparatus, at first, Ar, H_2, N_2 gas and a metallic compound gas, $TiCl_4$ gas are introduced in the second guide pipe 15 connected with the plasma generation chamber 1.

The plasma gas formed by the action of the electric field generated the microwave introduced through the wave guide 5 into the plasma generation chamber 1 and the magnetic field generated by the exciting coil 4, is introduced into the reaction chamber 2 by the divergent magnetic field generated by the exciting coil 4. And the plasma gas is provided on the surface of the sample 9, on which a TiN film is formed.

In this example, flow rate of Ar gas was 43 SCCM, that of N_2 gas was 15 SCCM, that of H_2 gas was 50 SCCM, and that of $TiCl_4$ gas was 10 SCCM; and temperature of the sample 9 was 600 °C.

Also in this example, almost the same film forming speed and were obtained as that in case of $TiCl_4$ gas flow rate of 10 SCCM shown in Fig. 3.

In Fig. 4, contrasted the examples 1,2 and the result of the experiment disclosed in Japanese Patent Laid-Open Publication No.3072/90 as a prior art, the relationship between aspect ratio and hole bottom / hole outside surface film forming speed is shown. It is obvious from Fig. 4 that at high aspect ratio, hole bottom / hole outside surface film forming speed is excellent.

Example 3

Next, an insulating film of SiO_2 was formed on a P-type Si substrate, wherein a contact hole was formed; by using the apparatus shown in Fig. 1 with the substrate as a sample, a thin film of TiN was formed on the inside surface of the contact hole.

At first, by operating exhaust system the pressure in the main body 3 was reduced to 1×10^{-6} Torr, after that, while $TiCl_4$ gas flow rate of 10 SCCM was supplied through the first guide pipe 13 into the reaction chamber 2, Ar: 43 SCCM, H_2: 50 SCCM, and N_2: 15 SCCM were supplied through the second guide pipe 15 into the plasma generation chamber 1. Under these conditions with changing gas pressure in the apparatus, the state of the TiN film formation especially the state of deposition of TiN film on the inside surface of the contact hole was investigated. As a result, at less than 2.0 mTorr the state of deposition was satisfactory, but at gas pressure of more than that unsatisfactory. A diagram based on the photomicrograph of the SEM scanning electron microscope, wherein a TiN film actually deposisited on the inside surface of the contact hole of aspect ratio 2, is show in Fig. 5. The deposition conditions were gas pressure 1.3 mTorr, microwave power 2.8kw, substrate temperature 550 °C, $TiCl_4$: 10 SCCM, H_2: 50 SCCM, N_2: 15 SCCM, and Ar: 43 SCCM.

It is regarded from Fig. 5 that a TiN film 33 deposisited on the side wall and bottom of the contact hole 35. The film thickness on the bottom was about 500 ~ 600 Å , and that on the side wall was 200 ~ 300 Å, while that on the insulating film was 1000Å. In other words, the thickness of film forming on the bottom of the contact hole 35 could be over 50 % of that on the substrate surface.

As comparative examples, diagrams based on the photomicrograph of SEM, wherein at pressure in the main body 3 of 3 mTorr and 5 mTorr, the other deposition conditions were the same, are shown in Figs. 6 and 7. Under these conditions, the state of sufficient deposition was not obtained.

Example 4

The diagram based on the photomicrograph of SEM in Fig. 8, shows the state of film formation under such conditions as pressure 0.7 mTorr, $TiCl_4$: 5 SCCM, Ar:H_2: 50 SCCM, N_2: 15 SCCM, microwave power 2.8kw, and substrate temperature 550 °C. It is obvious from this diagram that the thickness of film forming on the bottom of the contact hole 35 was 70 % of that on the substrate surface, very excellent percentage.

As obvious from Figs. 3 and 4, it is desirable that pressure in the main body 3 is set up at 2.0 mTorr, preferably less than 1.3 mTorr.

The plasma CVD method according to the present invention comprises activating gas by turning it into a plasma, introducing the activated gas along divergent magnetic flux line onto the sample, and forming a TiN film thereon. Accordingly, the activated gas molecules have orientation because of induced by the divergent magnetic field, and are irradiated on the sample almost vertically, resulting in that the TiN film on the surface of the insulation arround the contact hole and on the bottom of that gets thick, while the TiN film on the side wall of the contact hole gets thin. Since the TiN film is thick on the bottom of the contact hole, it has good barrier characteristic, while since the TiN film is thin on the side wall of the contact hole, the diameter of the contact hole doesn't get so small, resulting in not so high aspect ratio after the TiN film forming. As a result, in the next step, wherein electrode materials Al and W(tungsten) are filled in, probability of forming voids decreases, resulting in that highly reliable interconnection is possible.

In Fig. 9(a), the state of the TiN film 33 deposition arround the contact hole 35 by the plasma CVD method according to the present invention is shown, and later, the state after filling in with W(tungsten) is shown in Fig. 9(b). In addition, in Table 1, data of the film thickness formed by each film formation is shown.

Table 1

	Reactive Sputtering method	LPCVD method	E C R plasmaC V D method		
			5mTorr	1.3mTorr	0.7mTorr
film thickness on Si substrate	1000Å	1000Å	1000Å	1000Å	1000Å
film thickness on the side wall of the contact hole	200Å	1000Å	100Å	250Å	250Å
film thickness on the bottom of the contact hole	35Å	1000Å	300Å	500Å	700Å
barrier characteristic	×	○	△	○	○
void occurrence when tungsten filled in	× Because of much overhang on the upper	× As the actual aspect ratio is 3/1	○ The reason why the barrier characteriatics gets a	○	○

○ no voids occur × voids occur	corners, little tungsten can enter the hole	, it is dif ficult for tu ngsten to be filled in the hole.	little worse seems to be that the film thickness on bottom became thin 300 Å		

As described above, by the ECR plasma CVD method, a film formed on the bottom is thick, and in addition, in the next step of filling in with tungsten no voids occurs.

Example 5

A curve written with (●) in Fig. 10 indicates the relationship between the film resistivity of a thin film formed at microwave power 1kw, gas pressure 1.3 mTorr in the above-mentioned CVD apparatus and temperature of the substrate. That is, at the substrate temperature of more than 450°C, the film resistivity of a formed TiN film in comparison with 523 μ Ω cm, the value obtained by the LPCVD method described in a prior art, became less than 200μ Ω cm, very small value, which is very excellent value in view of the function of electrically connecting the diffusion layer part and the electrode part of metal interconnection in the semiconductor device. On the contrary, when the substrate temperature is less than 450°C, the film resistivityvalue of the formed TiN film abruptly increases, resulting in making the TiN film unsuitable for use.

Besides, a curve written with O in the Fig. 10 indicates the relationship between the forming speed of a TiN film and the substrate temperature under the conditions of microwave power 1kw and gas pressure 1.3 mTorr. The curve says that there is no special correlation between both of them. Consequently, it is better to keep the temperature of the substrate at more than 450°C, preferably 550°C.

Example 6

Fig. 11 indicates the relationship between microwave power and film forming speed (O) and that between microwave power and film resistivity (●). It was comfirmed from Fig. 11 that the specific resistance of less than 200μ Ω cm at the microwave power of more than 1kw, and less than 100 μ Ω cm at more than 2kw are obtained.

These results indicates that compared with the film resistivity 525μ Ω cm obtained by the LPCVD method of a prior art wherein only thermal reaction is used, the method according to the present invention, wherein both thermal reaction energy and plasma energy are used, is further excellent and that it is possible to achieve to the practical use level.

EXAMPLE 7

The diagrams based on the photomicrograph of SEM of a TiN film deposoted on the contact hole are shown in Figs. 12 ~ 15.

The deposition conditions are microwave power 1kw and the same as the deposition conditions shown in Fig. 5, except changing the flow rate of $TiCl_4$ gas. It was comfirmed from this Fig. 12 that the deposited TiN film doesn't have calum structure but homogenous fine structure. Accordingly, it was expected that it has a good barrier characteristic.

The cases of $TiCl_4$: 5 SCCM, $TiCl_4$: 15 SCCM, and $TiCl_4$: 20 SCCM are shown in Figs. 13, 14,and 15 respectively, which presents the change of the structure of the TiN Film was caused by changing the flow of $TiCl_4$. In Figs. 14 and 15, the TiN film has colum structure, while the TiN film in Fig. 13 has homogenous fine structure as well as that in Fig.12.

In the case of constant microwave power, as mentioned above, with increasing the flow rate of $TiCl_4$ gas, the structure of the TiN film tends to be colum, while in the case of increasing microwave power, even with the large flow rate of $TiCl_4$ gas, the structure of the TiN film can be homogenous and fine.

Next, the result of investigation of the relationship between microwave power, flow rate of $TiCl_4$ gas and structure of a TiN film.

Table 2

		flow rate of $TiCl_4$ (SCCM)			
		5	10	15	20
microwave power (kw)	1	○	○	×	×
	1.5	○	○	△	×
	2.0	○	○	○	×
	2.5	○	○	○	△
	2.8	○	○	○	○

○ : no cylindrical construction / barrier characteristic good

△ : some cylindrical construction occurs / " unstable

× : cylindrical construction occurs / " bad

It was regarded from this result that even if flow rate of $TiCl_4$ gas increased, correspondingly increasing microwave power can prevent occurence of colum structure.

Example 8

the result of the experiment showing the barrier characteristic is excellent, is shown in Fig. 16, wherein the curves of Al and Ti don't expand horizontally.

Fig. 16 is a graph indicating the result of analysis four samples as follows by RBS (Rutherford Backscattering Spectroscopy);

a TiN film of 1000Å formed on a Si substrate, with Al deposited thereon, (1) unheated, (2) heated at 500 °C for 30 minutes, (3) at 600 °C for 30 minutes, and (4) at 650 °C for 30 minutes. RBS comprises the steps of irradiating He atoms of a definite energy on the substrate, and by the energy of the reflecting He investigating the element distribution to the direction of the film thickness in the film. The energy loss of He which collided with every element is determined by element (atomic weight), that is, the lighter the element is, the lighter it goes. Accordingly, although the film construction is Al/TiN/Si, the peaks come in the order of Si, Ti, and Al. Besides, the width of each peak corresponds to the film thickness, so that a wide peak means diffusion (as Si is a substrate and wide, only the one side can be seen). It is obvious from Fig. 16 that the peaks make almost no change by heat treatment, and that even after the heat treatment at 650 °C for 30 minutes, it shows high barrier characteristic (effect of preventing diffusion).

A diagram at the upper part in the frame indicates that in the film structure Al/TiN/Si, He was irradiated from the direction of Al, and the yield of He ions scattering backward was measured.

In the next step after forming a TiN film, wherein the interconnction of W alloy or Al or Al alloy such as Al-Si-Cu is done on the TiN film, when chlorine remains in the TiN film, the interconnection of Al and the like is heavily corroded by the chlorine. In some cases, $AlCl_3$ insulating film is produced, resulting in the corrosion of the Al interconnection to the extent to which it is observed with the naked eye. Therefore, it is an indispensable step to decrease chlorine from a TiN film as much as possible.

Figs. 17 and 18 shows the EDX (Energy Dispersion-type X-ray analyzer) spectra of the TiN films formed at the microwave power of 1kw and 2.8kw, under the same deposition conditions as those in the examples according to the present invention. At the microwave power of 1kw, the peak of chlorine Cl was noticed, while at 2.8kw no peak of chlorine Cl was noticed.

Thus the contamination of chlorine Cl can be checked by enhancing the microwave power. In addition, chlorine Cl can be reduced by the H_2 plasma treatment after the TiN film formation.

Fig. 19 indicates the result analyzed by SIMS (Secondary Ion Mass Spectroscopy) from the surface of the sample given the H_2 plasma treatment after the TiN film formation to the direction of depth (vertically to TiN film toward the Si substrate).

The SIMS comprises the steps of digging the film to the direction of depth by irradiating oxygen ions and measuring the distribution of elements or molecules (e.g. TiN) existing in the direction of the depth. In other words, irradiating the high energy oxygen ions so that materials in the film are expelled, and analusis the signal strength of the ions (the secondary ions) in the direction of depth.

In Fig. 19, the left side (on the vertical axis) is the surface side of a TiN film, and as going to the right, the depth digged down becomes bigger. On the surface of the film, chlorine was reduced by the H_2 plasma treatment after the TiN film formation.

Thus, by the H_2 plasma treatment, chlorine concentration on the surface of the TiN film can be reduced, resulting in preventing the corrosion of Al interconnection and the like by chlorine. The H_2 plasma treatment is to stop supplying Ti compound gas such as $TiCl_4$ and N_2 gas at the end of the treatment of the TiN film formation, and to supply Ar gas and H_2 gas in order to keep the state wherein a plasma is produced.

Next, X-ray diffraction pattern of TiN film formed by the method according to the example is shown in Fig. 20. The pattern diagram indicates the crystal of TiN oriented on the Si substrate (111) only in the direction (100). The deposition conditions were microwave power 1kw, substrate temperature 550 °C, flow of N_2: 15 SCCM, H_2: 50 SCCM, and Ar: 43 SCCM.

(100) oriented film has an excellent barrier characteristic, and it is guessed that extremely strong (100) orientation of a TiN film formed by the method according to the example may be based on the directionality of a plasma.

As obvious from the above-mentioned explanations, by the method for forming a thin film according to the present invention, it is capable of forming a metal nitride film having good Step Coverage, and forming a thin film sufficiently keeping a barrier characteristic on the contact hole, even if a LSI device gets more highly integrated and aspect ratio of the contact hole formed on a insulation layer becomes bigger.

In addition, the film thickness of the thin film formed on the side wall of the contact hole can be made thinner than that on the bottom of the contact hole, and with keeping a barrier characteristic on the bottom of the contact hole, aspect ratio of the contact hole after forming a thin film can be refrained from enhanced. Accordingly, in the following step of filling in with interconnection materials, no voids occur in the contact hole, resulting in preventing interconnection from broken and improving reliability of a LSI device.

Besides, it is possible to form a thin film at such low temperature as no bad influence is given on producing a LSI device, and in addion, with no particles such as yellow powder produced, to produce further reliable LSI devices.

Claims

1. A method for generating a thin film, comprising the steps of:
generating a plasma in a plasma generation chamber by action of an electric field generated by a microwave and a magnetic field generated by an exciting coil arranged around; and
introducing the generated plasma into a reaction chamber, resulting in forming a thin film on a sample placed on a sample stage, wherein it is a characteristic to form a metal nitride film on said sample, by introducing Ar, H_2, and N_2 gas into said plasma generation chamber, while introducing a metallic compound gas into said reaction chamber.

2. A method for forming a thin film, comprising the steps of:
gentrating a plasma in a plasma generation chamber by action of an electric field generated by a microwave and a magnetic field generated by an exciting coil arranged around; and
introducing the generated plasma into a reaction chamber, resulting in forming a thin film on a sample placed on a sample stage, wherein it is a characteristic to form a metal nitride film on said sample, by introducing Ar, H_2, N_2 gas and said metallic compound gas into said plasma generation chamber.

3. A method according to Claims 1 or 2, wherein, on a substrate for producing a semiconductor device on which an insulating film having a contact hole thereon is formed, by using titanium tetrachloride gas as a metallic gas, under the conditions that pressure in the reaction chamber is less than 2.0 mTorr and temperature of said substrate, a sample is more than 450°C, a Ti nitride film is formed on the contact hole.

4. A method according to Claims 1 or 2, wherein, on a substrate for producing a semiconductor device on which an insulating film having a contact holethereon is formed, by using titanium tetrachloride gasas a metallic compound gas, under the conditions that pressurein the reaction chamber is less than 1.3 mTorr and temperature of said substrate, a sample, is high than 450°C, a Ti nitride film is formed on the contact hole.

5. A semiconductor device, wherein thickness of a Ti nitride film on the bottom of a contact hole is thicker than that on the side wall of said contact hole.

6. A semiconductor device, wherein thickness of a Ti nitride film on the side wall of a contact hole is 20 ~ 60 % of that on the bottom of said contact hole.

7. A method according to Claims 1 or 2, wherein a thin film is formed with applying RF to a microwave inlet window.

8. A method according to Claims 3 or 4, wherein a thin film is formed with applying RF to a microwave inlet window.

9. A semiconductor device, wherein by means of introducing Ar, H_2 and N_2 gas into a plasma generation chamber, while introducing titanium tetrachloride gas into a reaction chamber, forming a plasma in said plasma formation chamber, by action of an electric field generated by a microwave and a magnetic field generated by an exciting coil arranged around, and introducing the generated plasma into said reaction chamber, thickness of a Ti nitride film formed on the bottom of a contact hole was made thicker than that on the side wall of the contact hole.

10. A semiconductor device, wherein by means of introducing Ar, H_2, N_2 gas and titanium tetrachloride gas into a plasma generation chamber, generating a plasma in said plasma generation chamber by action of an electric field generated by a microwave and a magnetic field generated by an exciting coil arranged around, and introducing the generated plasma into said reaction chamber, thickness of a Ti nitride film formed on the bottom of a contact hole was made thicker than that on the side wall of the contact hole.

11. A semiconductor device, wherein by a method according to Claim 3, thickness of a Ti nitride film formed on the bottom of a contact hole was made thicker than that on the side wall of the contact hole.

12. A semiconductor device, wherein by a method according to Claim 4, thickness of a Ti nitride film formed on the bottom of a contact hole was made thicker than that on the side wall of the contact hole.

13. A semiconductor device, wherein by means of introducing Ar, H_2 and N_2 gas into a plasma generation chamber, while introducing titanium tetrachloride gas into a reaction chamber, generating a plasma in said plasma generation chamber, by action of an electric field generated by a microwave and magnetic field generated by an exciting coil arranged around, and introducing the generated plasma into said reaction chamber, thickness of a Ti nitride film formed on the side wall of a contact hole was made 20 ~ 60 % of that on the bottom of the contact hole.

14. A semiconductor device, wherein by means of introducing Ar, H_2, N_2 gas and titanium tetrachloride gas into a plasma generation chamber, generating a plasma in said plasma generation chamber, by action of an electric field generated by a microwave and a magnetic field generated by an exciting coil arranged around, and introducing the generated plasma into said reaction chamber, thickness of a Ti nitride film formed on the side wall of a contact hole was made 20 ~ 60 % of that on the bottom of the contact hole.

15. A semiconductor device, wherein by a method according to Claim 3, thickness of a Ti nitride film formed on the side wall of a contact hole was made 20 ~ 60 % of that on the bottom of the contact hole.

16. A semiconductor device, wherein by a method according to Claim 4, thickness of a Ti nitride film formed on the side wall of a contact hole was made 20 ~ 60 % of that on the bottom of the contact hole.

17. A method according to Claims 1 or 2, wherein H_2 plasma treatment is carried out after forming a Ti nitride film.

FIG. 1

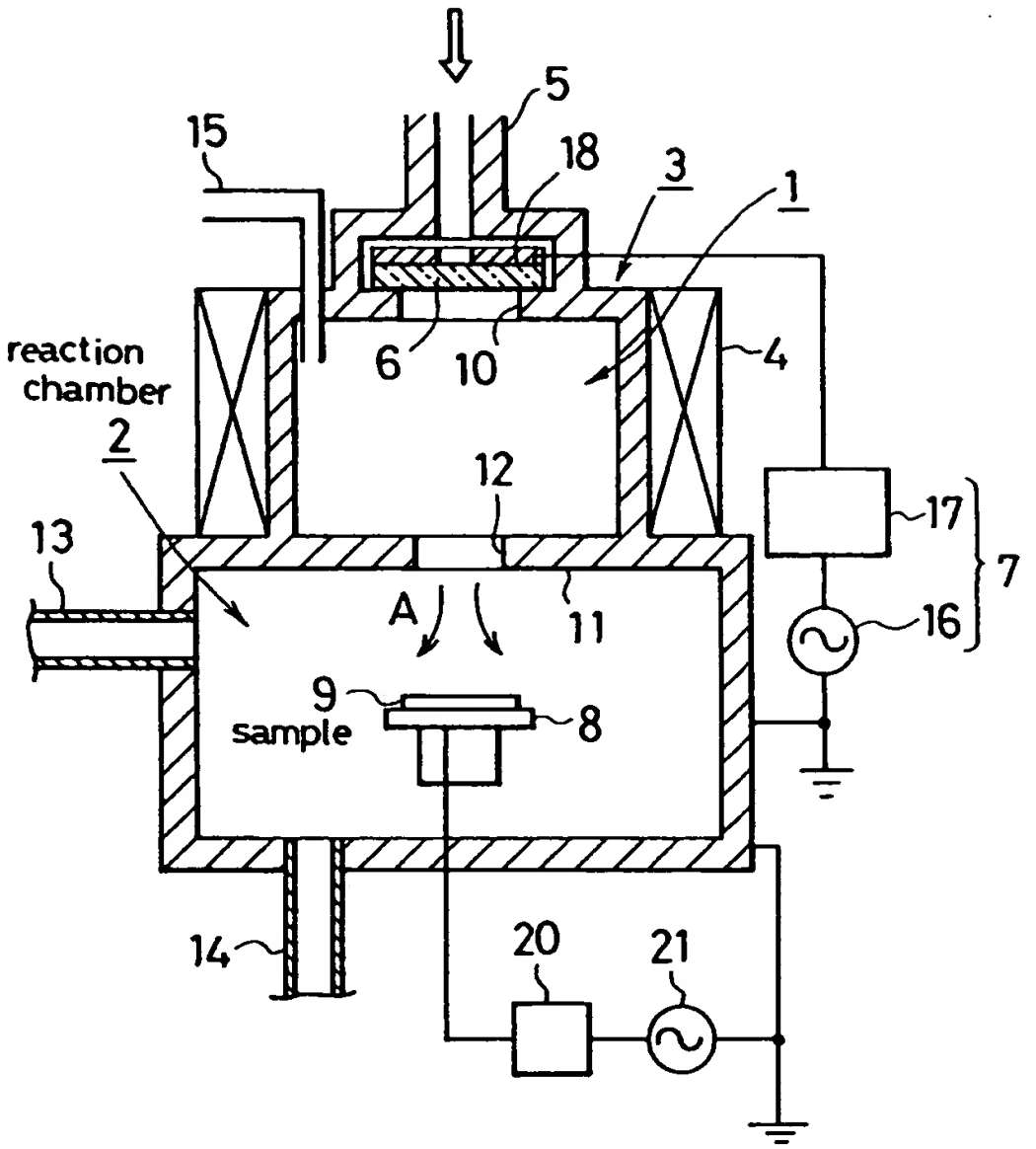

5
15
18
3
1
reaction chamber
2
6
10
4
12
13
17
7
A
11
16
9
sample
8
14
20
21

FIG. 2

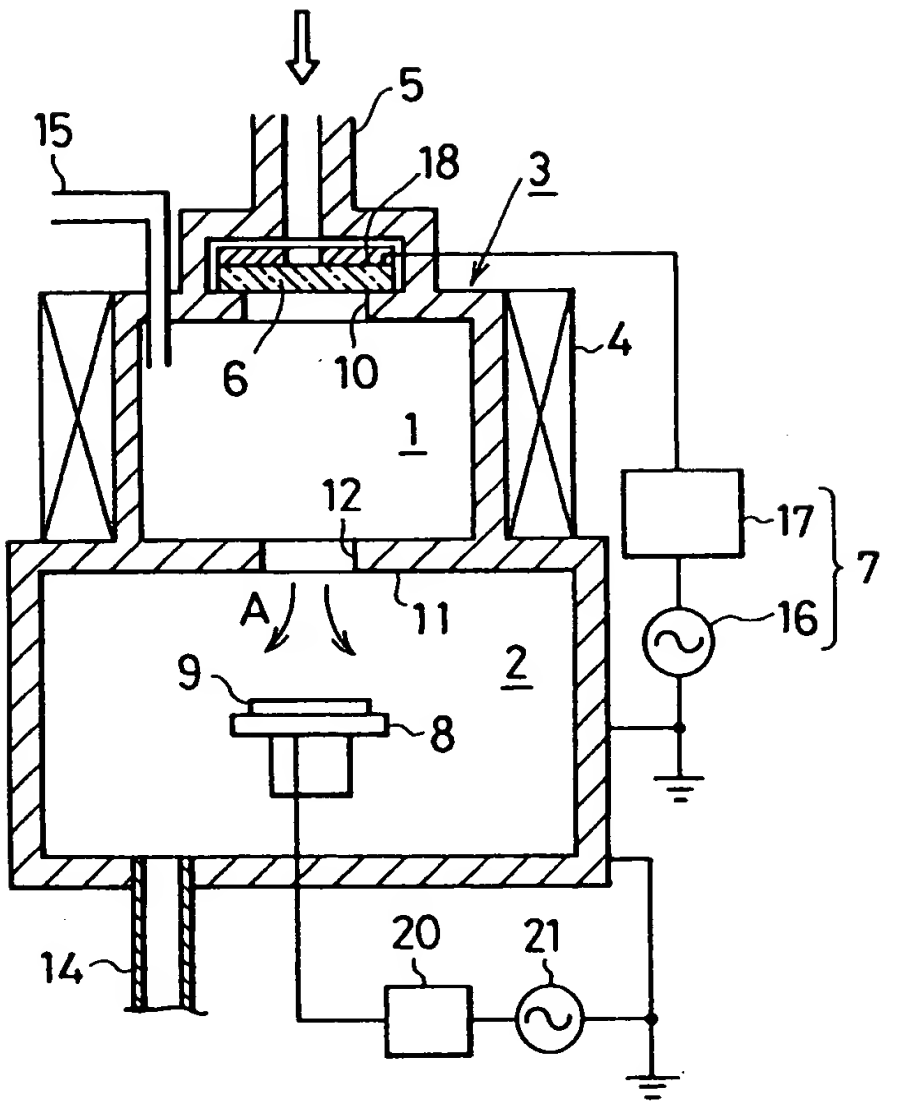


FIG. 3

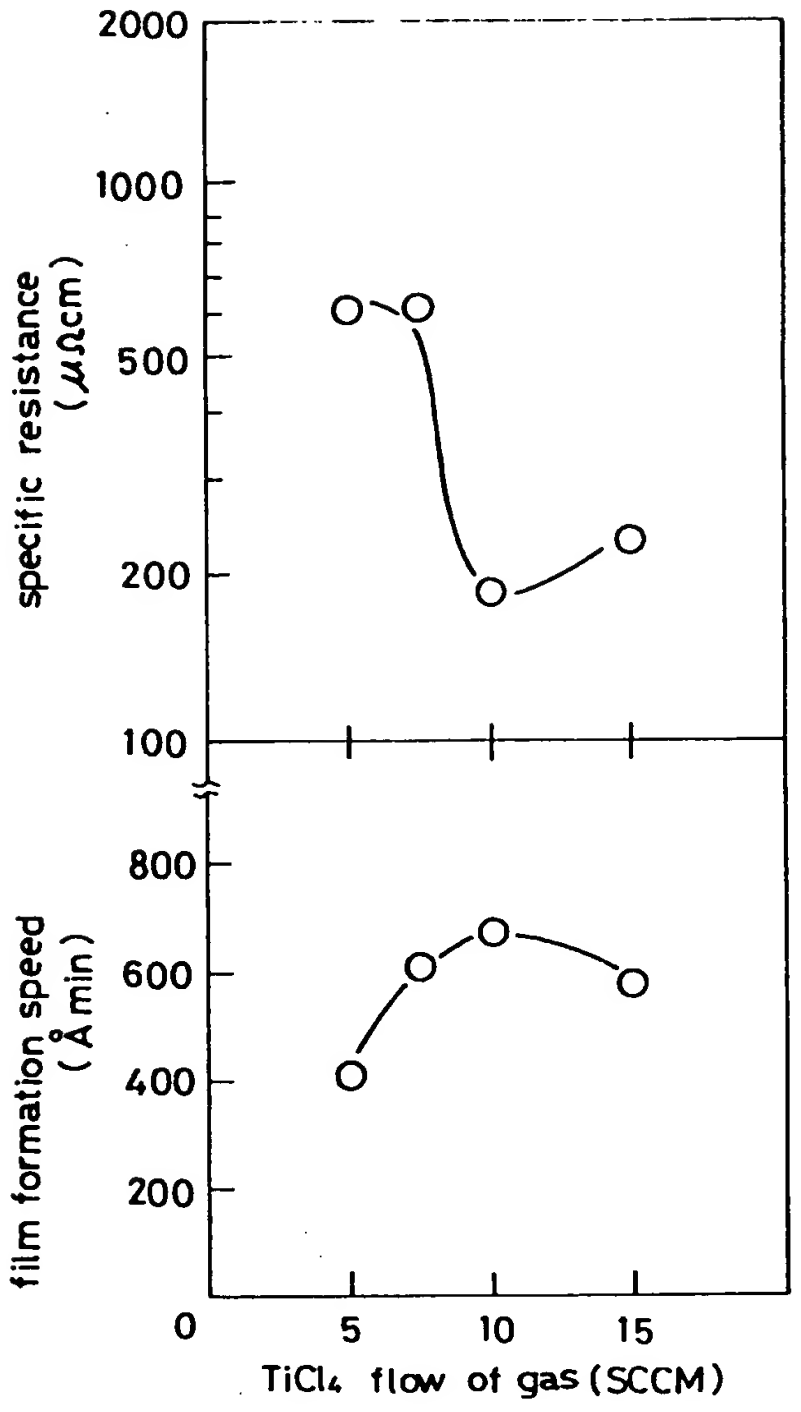

2000
1000
500
200
100
specific resistance
(μΩcm)
800
600
400
200
0
film formation speed
(Å/min)
5
10
15
TiCl4 flow of gas (SCCM)

FIG. 4

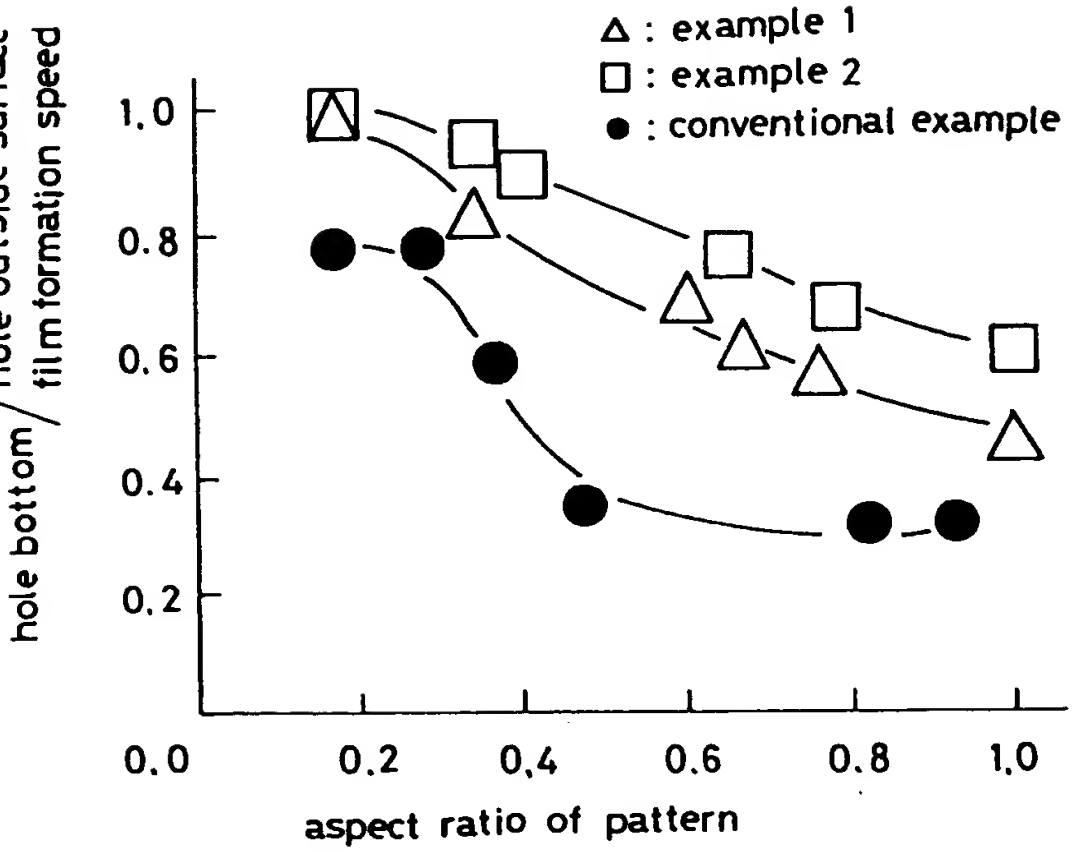

△ : example 1
□ : example 2
● : conventional example
hole bottom / hole outside surface
film formation speed
1.0
0.8
0.6
0.4
0.2
0.0
0.2
0.4
0.6
0.8
1.0
aspect ratio of pattern

FIG. 5

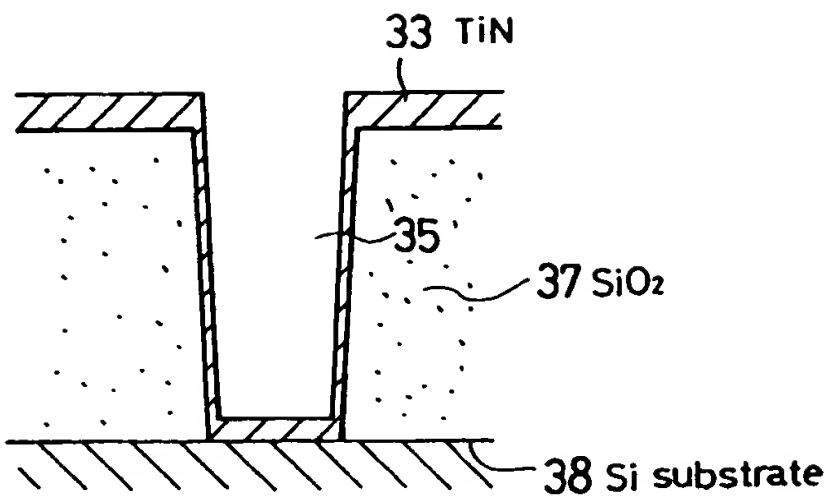


FIG. 6

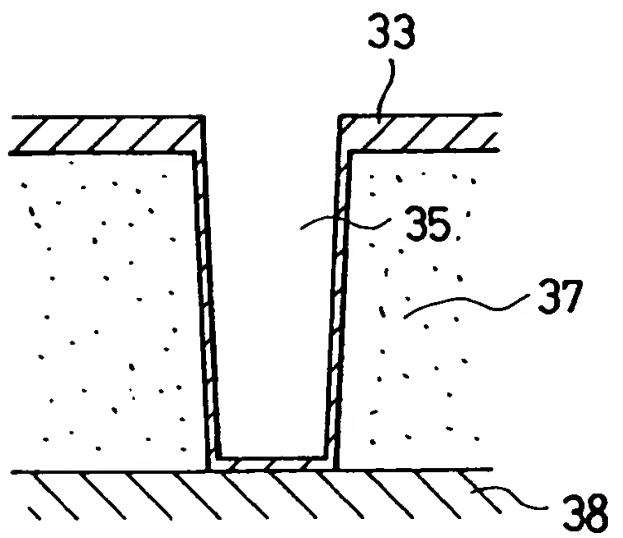


FIG.7

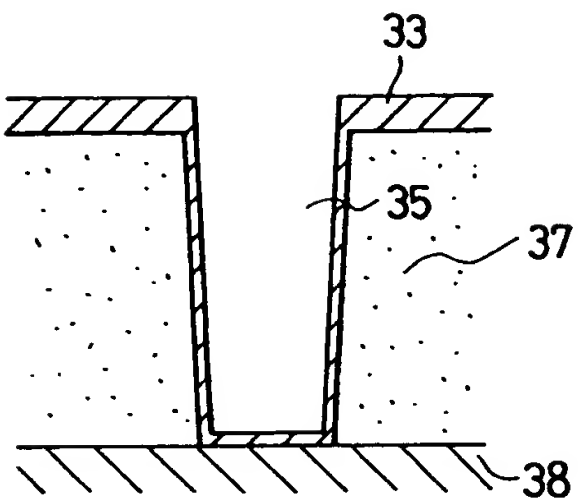


FIG.8

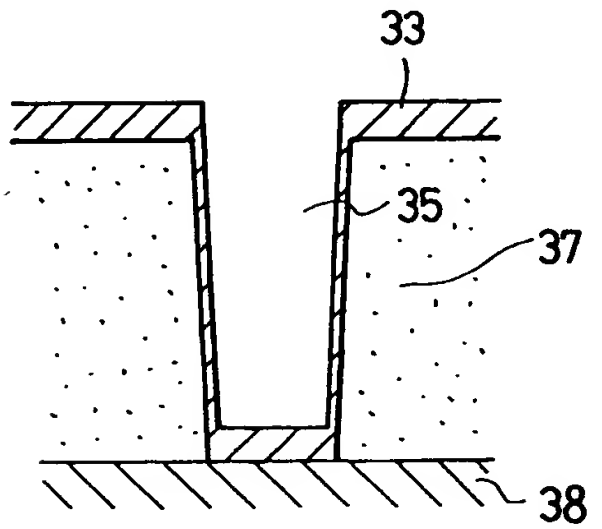


FIG. 9

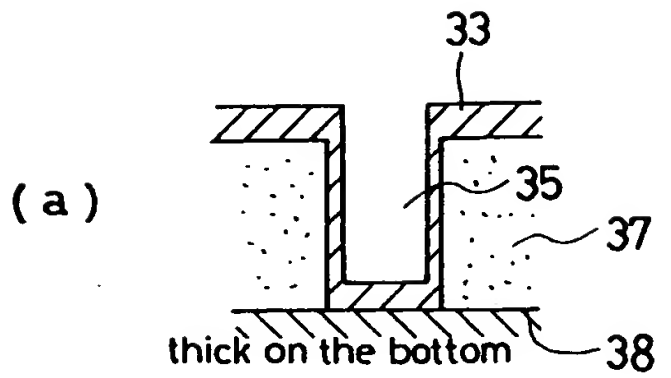


FIG. 10

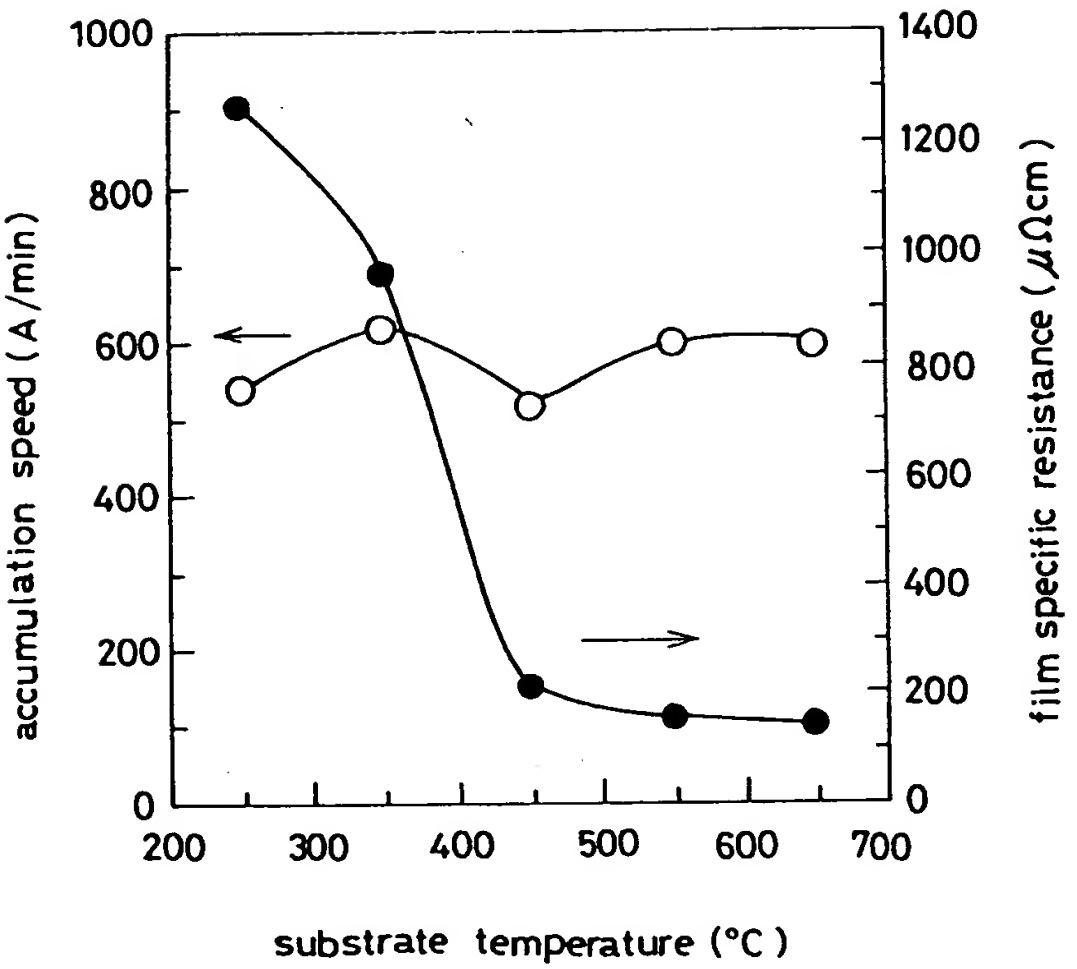

1000
800
600
400
200
0
1400
1200
1000
800
600
400
200
0
200
300
400
500
600
700
accumulation speed (A/min)
film specific resistance (μΩcm)
substrate temperature (°C)

FIG. 11

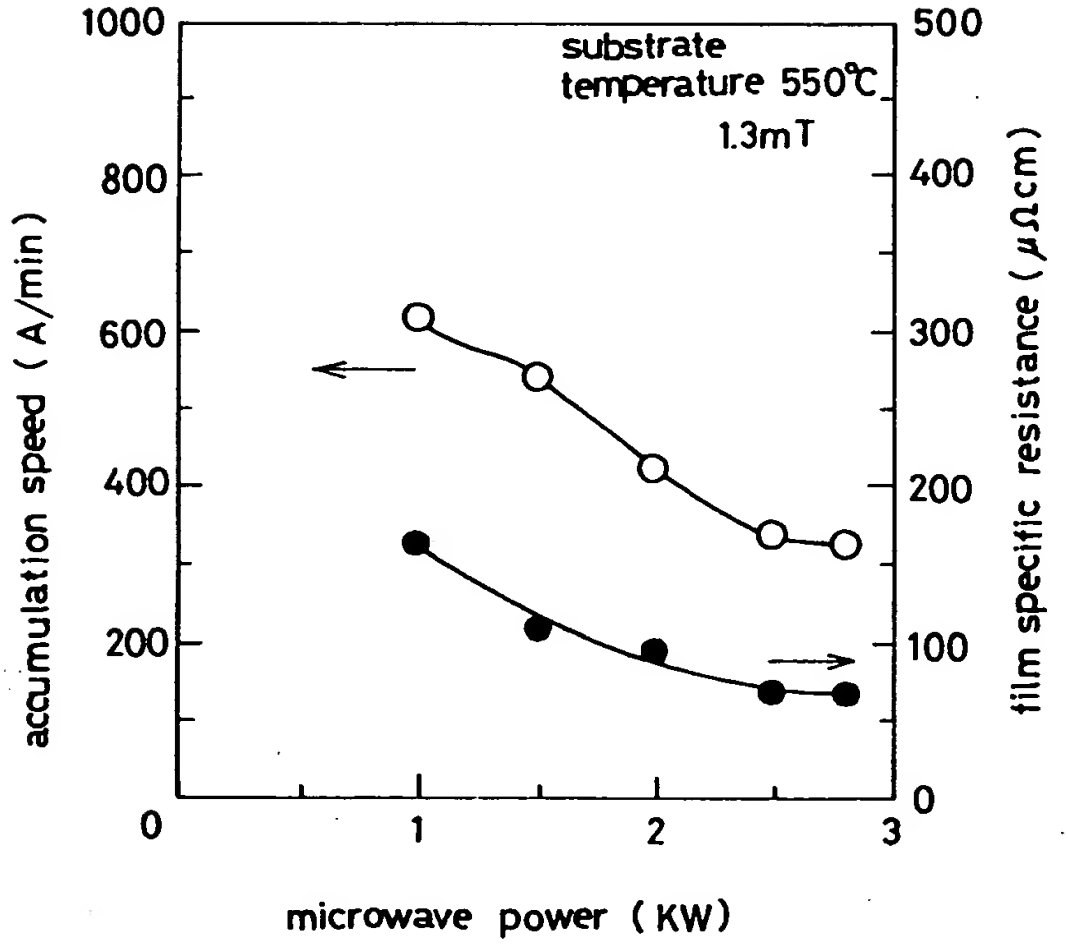

substrate
temperature 550℃
1.3mT
accumulation speed (A/min)
film specific resistance (μΩcm)
microwave power (KW)
1000
800
600
400
200
0
500
400
300
200
100
0
1
2
3

FIG. 12

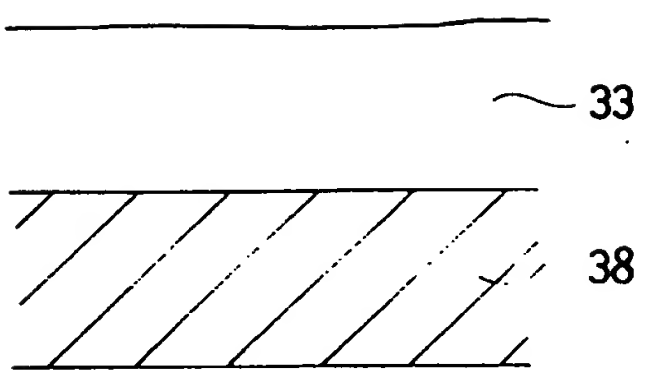


FIG. 13

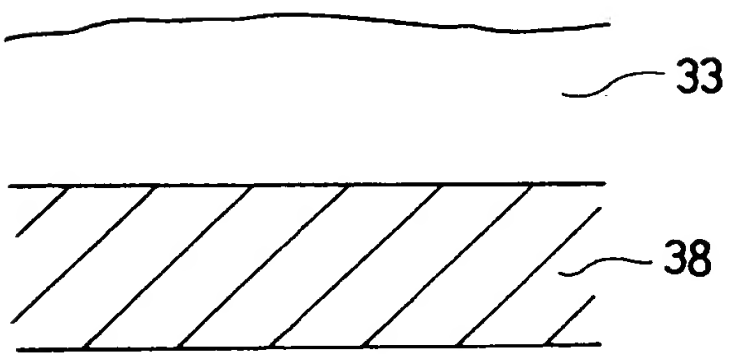


FIG. 14

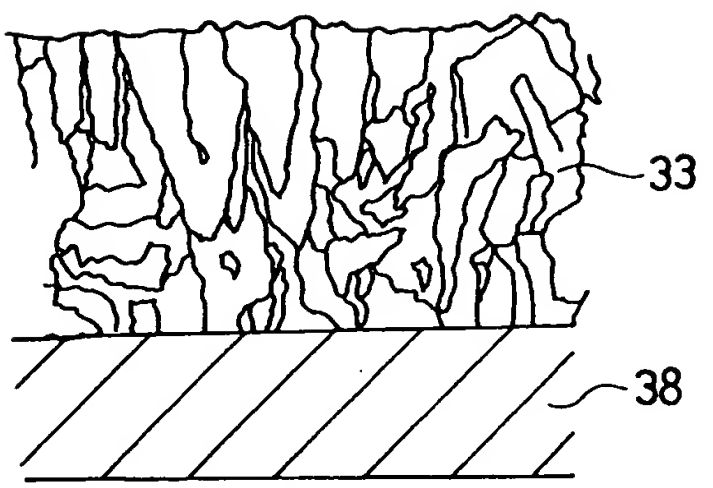


FIG. 15

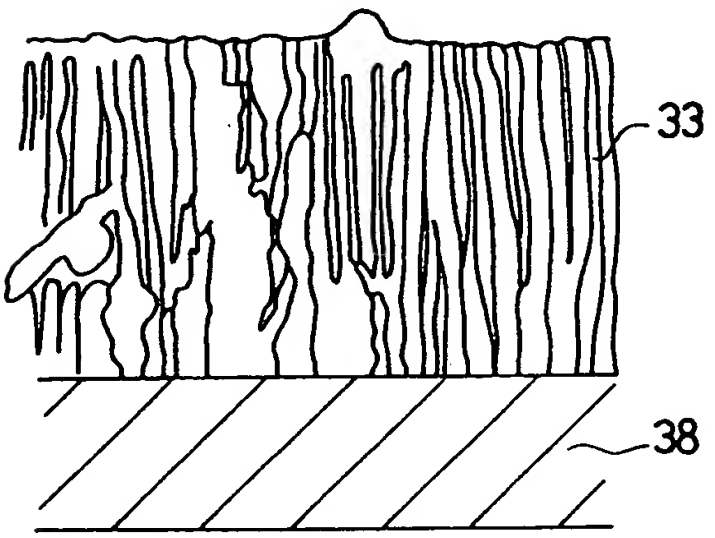


FIG. 16

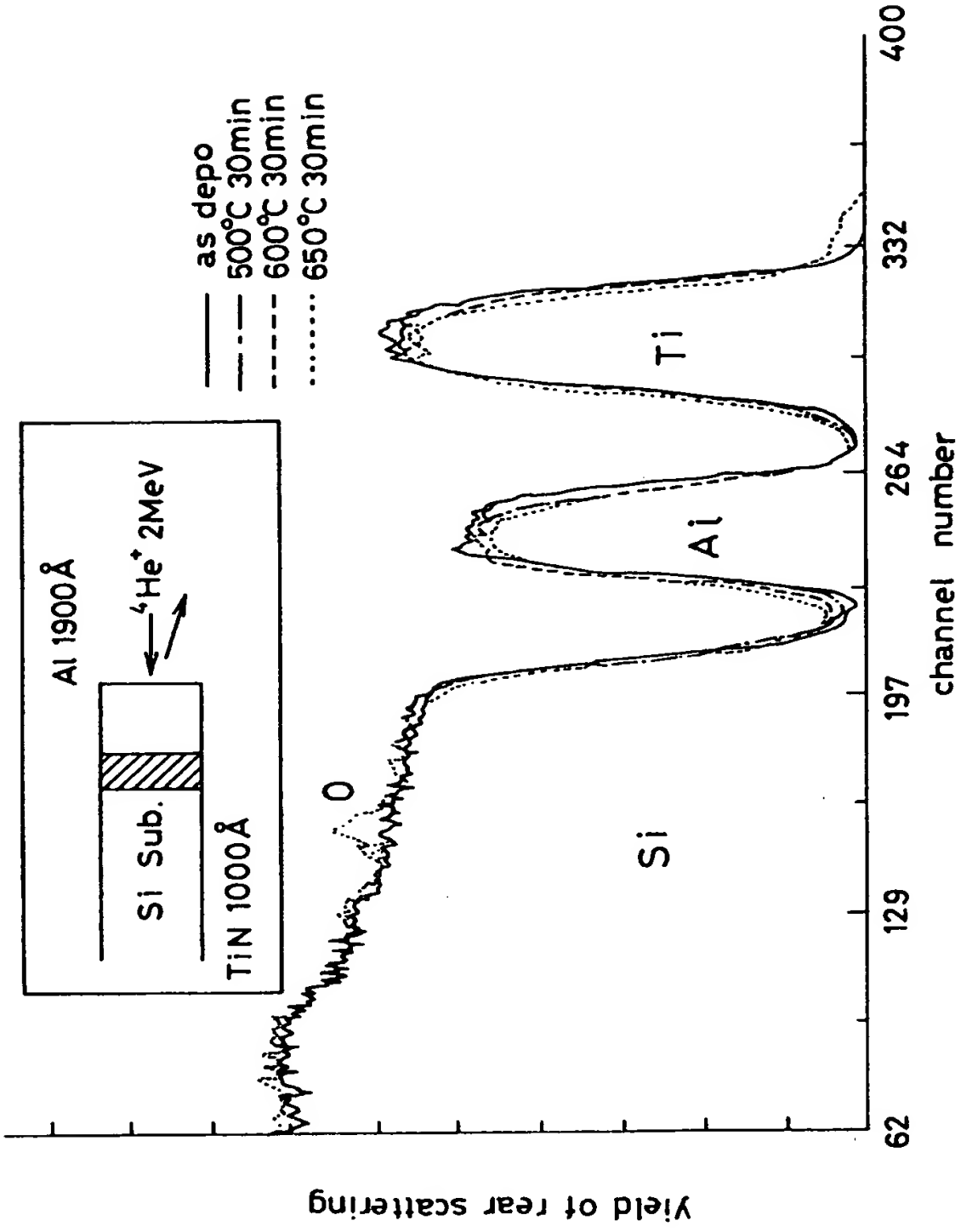

as depo
500°C 30min
600°C 30min
650°C 30min
Al 1900Å
$^4He^+$ 2MeV
Si Sub.
TiN 1000Å
O
Ti
Al
Si
Yield of rear scattering
channel number
62
129
197
264
332
400

FIG. 17

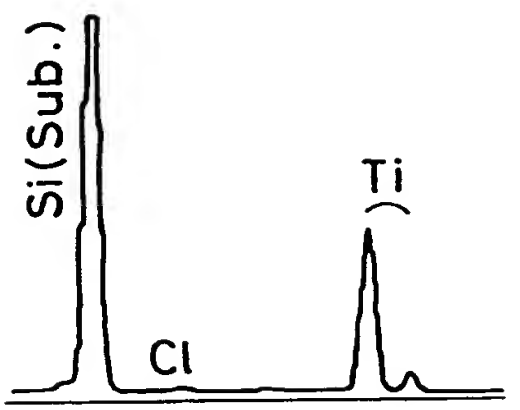


FIG. 18

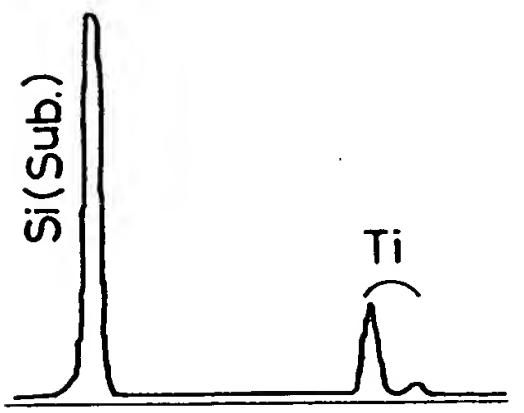


FIG. 19

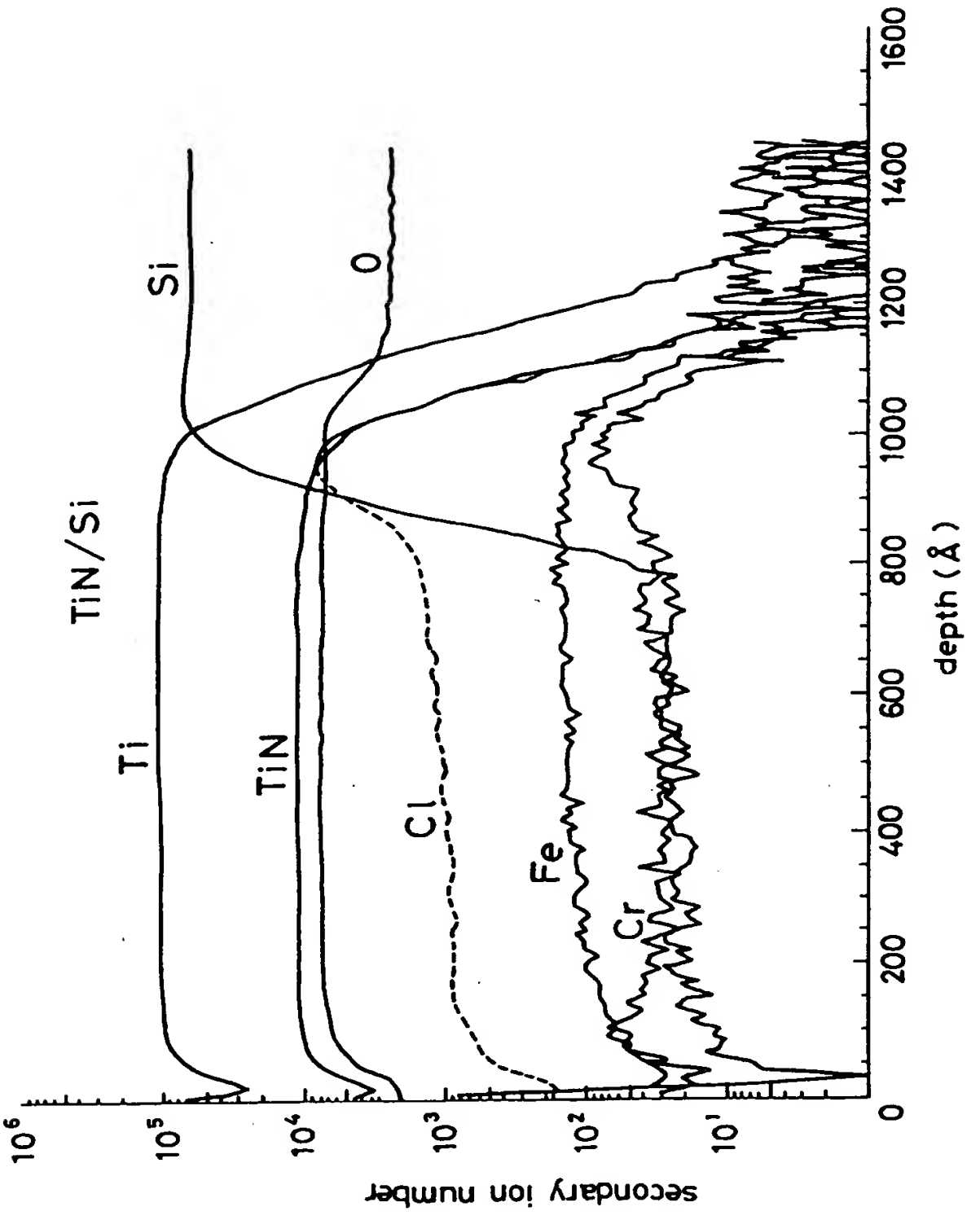
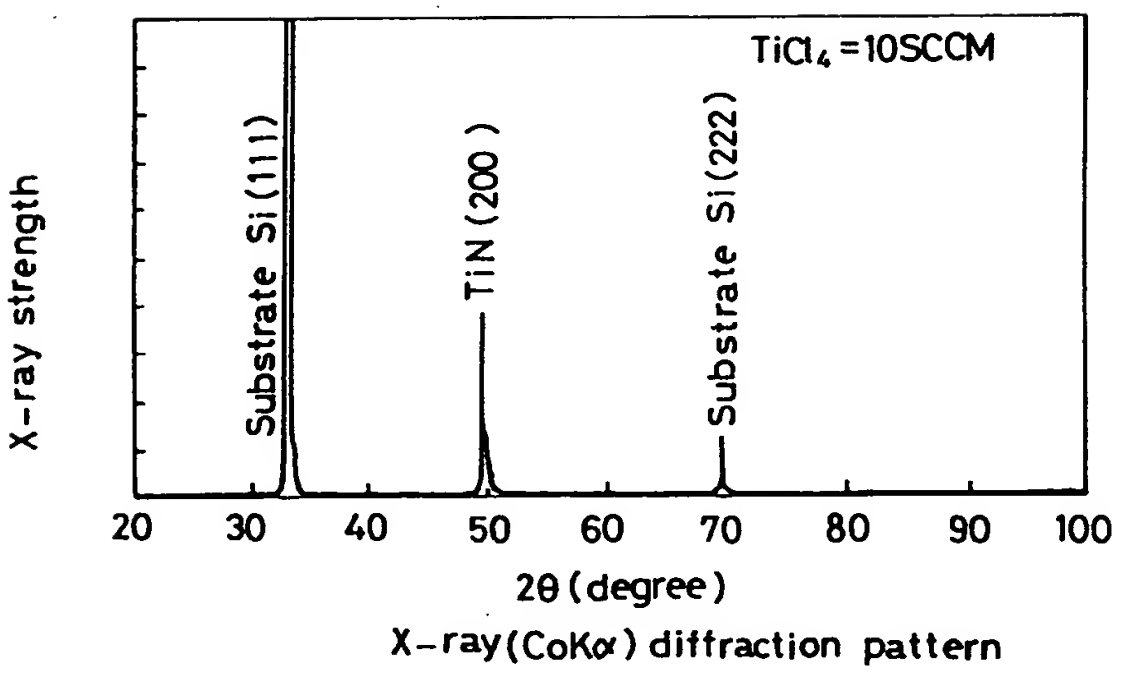

TiN/Si
Si
O
Ti
TiN
Cl
Fe
Cr
TiN
secondary ion number
depth (Å)
10^6
10^5
10^4
10^3
10^2
10^1
0
200
400
600
800
1000
1200
1400
1600

FIG. 20



X-ray(CoKα) diffraction pattern

FIG. 21

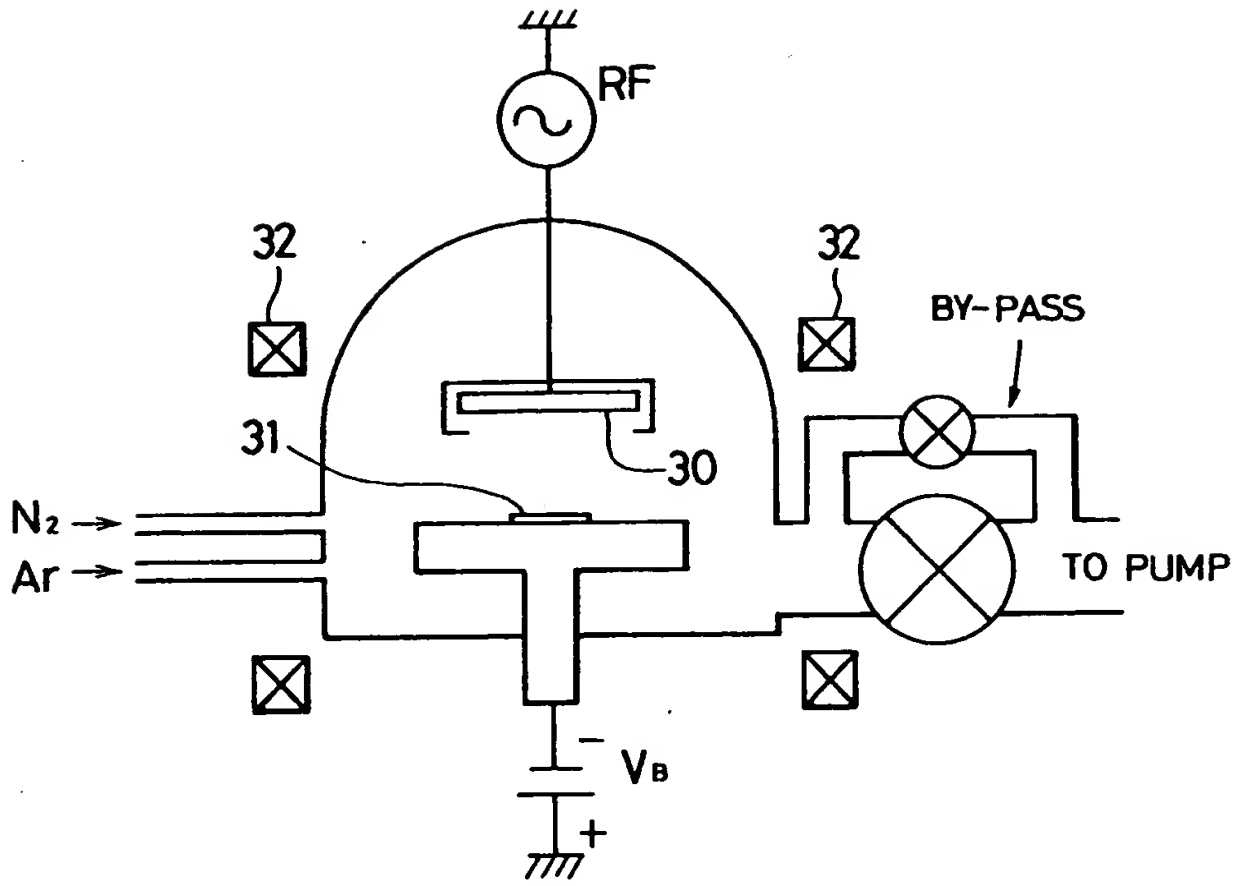

RF
32
32
BY-PASS
31
30
N_2
Ar
TO PUMP
V_B
−
+

FIG. 22

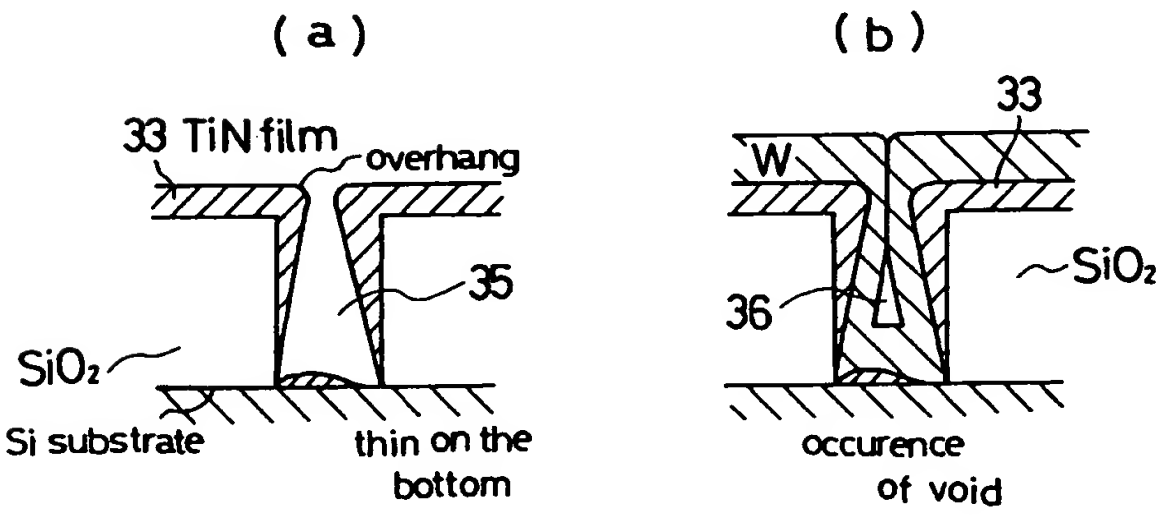

(a)
33 TiN film
overhang
35
SiO_2
Si substrate
thin on the bottom
(b)
33
W
SiO_2
36
occurence of void

FIG. 23

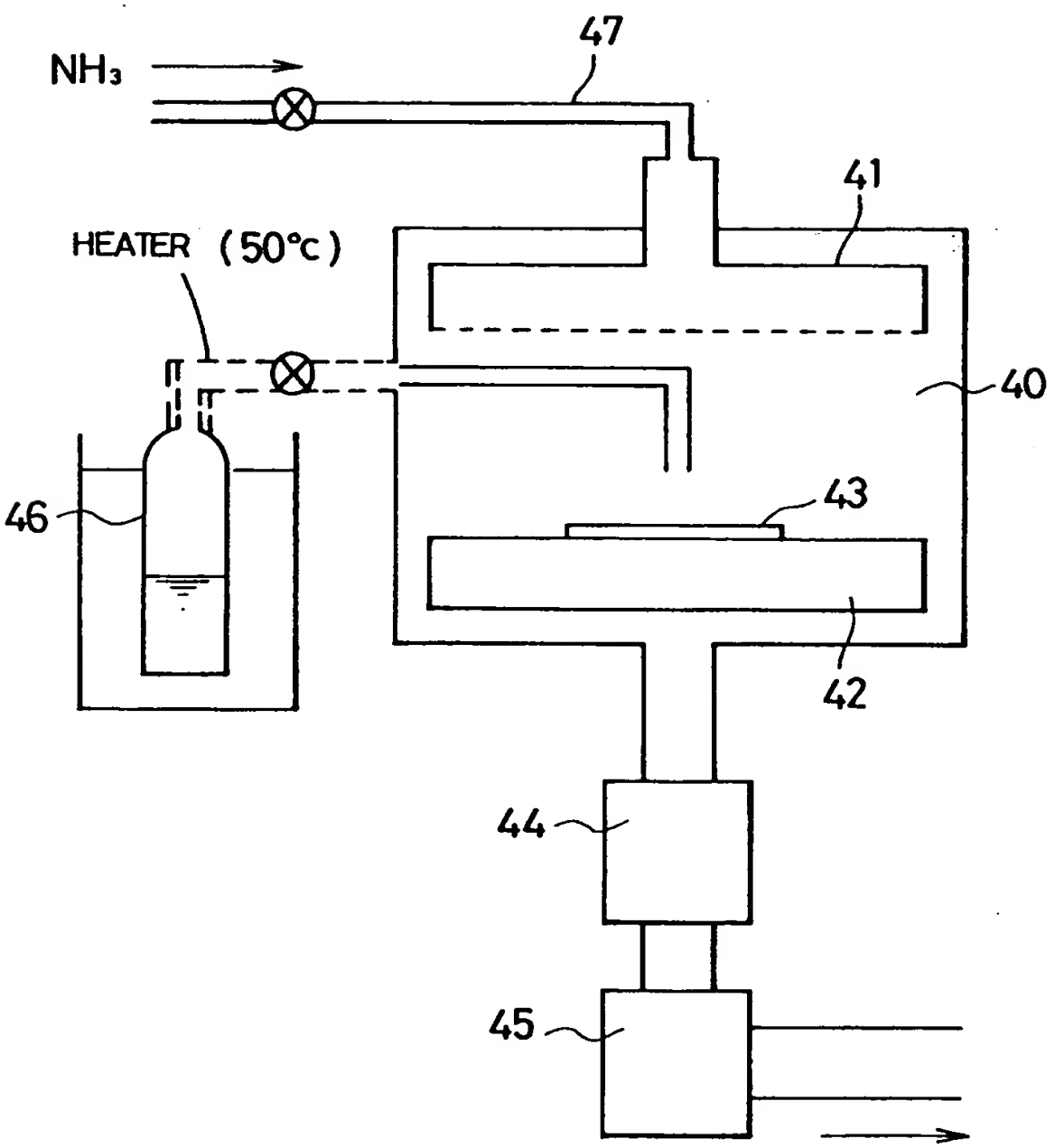
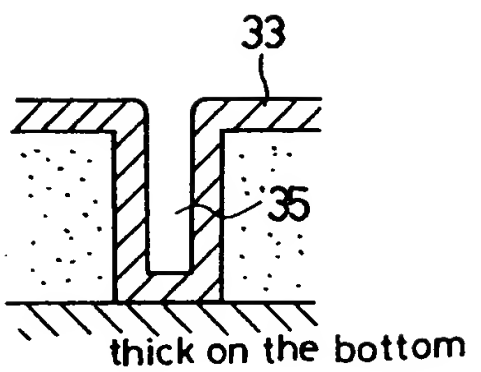


FIG. 24

(a)



(b)